

QUANTITATIVE ELEMENTAL PROFILING IN OPTICAL EMISSION SPECTROSCOPY

CROSS-REFERENCE TO RELATED APPLICATIONS

This nonprovisional application is a continuation-in-part of and claims priority to U.S. Nonprovisional application Ser. No. 14/334,206, entitled “Quantitative Elemental Profiling in Optical Emission Spectroscopy”, filed Jul. 17, 2014, which is a continuation of and claims priority to provisional application No. 61/847,370, entitled “Quantitative Elemental Profiling in Optical Emission Spectroscopy”, filed Jul. 17, 2013, both of which are incorporated herein by reference in their entireties.

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

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BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates, generally, to spectral analysis. More specifically, it relates to the normalization of line assignments in spectral analysis to accurately determine confidence levels of identity of elements represented by said line assignments.

2. Brief Description of the Prior Art

Spectroscopic techniques based on emission (LIBS, ICP-OES, GD-OES, Arc, Spark, etc.), rely on the assignment of the spectral peaks in a spectrum to know the composition of the material that is analyzed. The assignment of these peaks is done by looking up the peaks in a database that usually contains information, such as (1) the position of the peak in the spectrum (wavelength, wavenumber, energy, etc.); (2) the origin of the peak (emitter, absorber, vibrational mode, etc.); (3) the strength of the absorption/emission/scattering (Einstein coefficients, cross section, oscillator strength, etc.); and (4) additional technical details on the physics of the transition.

The spectral analysis is typically performed by either a practitioner or an algorithm. However, there is no quantitative evaluation of the quality of this assignment. This evaluation of the level of confidence (LOC) can be utilized in the ongoing question of accuracy and precision of assignment of a spectral line in the spectrum. What is needed is a technology that establishes such level of confidence.

The conventional art provides only the line assignment without a factor to judge the confidence in this assignment. This lack of a measure of confidence prevents a complete trust in the case of low resolution and forces the user or operator to rely on the experience, training, and skill set of a practitioner.

An example of optical emission spectroscopy, the LIBS technique, provides spectra for the possible identification and classification of compositions, such as pollutants. The use of the spectral lines in the spectrum relies on the assignment of these lines to the emitter at the origin of the emission. This assignment is done by a practitioner or an algorithm by analyzing a database for the position of the peak, its emitter and its probability (absolute or relative) of emission. However, conventional LIBS technology relies on

low resolution spectra (10 pm), non-adapted databases, dynamic plasma (broadening and shifts of spectral lines [W. Hübert, G. Ankerhold, “Elemental misinterpretation in automated analysis of LIBS spectra”, *Analytical and Bioanalytical Chemistry* 400(10), 3273-3278 (2011)]), and a lack of protocol (i.e., the specimen type and apparatus used affects the resultant detection limits, and as such, accuracy and precision can change from test to test depending on these factors). There is, thus, a need for a level of confidence in LIBS line assignment—an aspect that the conventional art has not contemplated.

Regarding the low resolution and interference relied upon by LIBS technology, the spectral resolution of the LIBS instrument is typically in the order of 0.01 to 0.05 nm pixel-to-pixel, in order to detect several spectral lines and still remain compact. This means that the spectral resolution is usually 0.03 to 0.15 nm. The MIT wavelength tables [G. R. Harrison, “Massachusetts Institute of Technology Wavelength tables” (1969)] establish that for “line-classification purposes”, the wavenumber of a line must be known within 0.02 cm^{-1} (0.02 pm for an emission at 300 nm). Even with attempts to increase this resolution by data processing [B. O’Leary, J. A. Kelley, “Utilization of the coherence function with Welch’s method for signal analysis in low resolution laser-induced breakdown spectroscopy”, *Applied Spectroscopy* 64(4), 370-376 (2010)], the LIBS instruments then are not suitable for an indisputable line assignment. As a result, spectral interferences are nearly unavoidable. Furthermore, the plasma conditions can involve broadening and shift of the spectral lines.

Typical databases used in optical emission spectroscopy are the MIT [G. R. Harrison, “Massachusetts institute of Technology Wavelength tables” (1969)] and NIST [ASD Data Lines Levels, National Institute of Standards and Technology: Physical Measurement Laboratory, March 1999] spectral databases, which were established by arc spectrochemical excitation. The Kurucz database, based on an atomic and molecular code, is also used.

Additionally, there is a lack of precision in tables for spectral analysis since analysis is generally qualitative. As discussed by NIST itself [ASD Data Lines Levels, National Institute of Standards and Technology: Physical Measurement Laboratory, March 1999], relative intensities are noted by authors of each publication, and thus, there is no common scale for these relative intensities. The different authors provide and use different scales, and so the relative intensities only have a meaning within the given scale or spectrum (i.e., within the spectrum of a given element in a given stage of ionization). Further, relative intensities are dependent on the light source used for the excitation. Also, the relative intensities are primarily useful for comparing strengths of spectral lines that are not widely separated, since there generally is no correction for spectral sensitivity of the measuring instruments (spectrometers, photomultipliers, photographic emulsions). Furthermore, the majority of these values are based on the MIT wavelength tables [G. R. Harrison, “Massachusetts Institute of Technology Wavelength tables” (1969), page xii], where the author explains how highly non quantitative their procedure is and where the procedure is based on “eye estimates of the lines made by observing them on a screen”. In the case where the authors did not themselves measure the lines, they “adjusted the intensity values to fit [their] scale as best as [they] could”, it then becomes obvious that a quantitative measure of the level of confidence cannot rely on such relative intensity values.